IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of Takuo HIBI et al.

Serial No. : 09/249,100 Group Art Unit : 1754

Filed : February 12,1999 Examiner : N. M. Nguyen

For : PROCESS FOR PRODUCING CHLORINE

* * * * *

DECLARATION UNDER 37 C.F.R. § 1.132

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

Sir:

I, Takuo HIBI, a Japanese citizen residing at 5-9-6, Goinishi, Ichihara-shi, Chiba, Japan,

Declare:

That I graduated from Tohoku University, Department of applied chemistry, Faculty of Engineering in March 1978, graduated from master course of that and entered Sumitomo Chemical Company, Limited in April 1980, in which company I have since then been engaged in study of catalyst-development for petrochemicals;

That I am one of the inventers of the identified-application;

That the following experiment was conducted by me or under

my direct supervision.

EXPERIMENT

A catalyst was prepared by the following process. That is, 20.0 g of a titanium oxide powder (PT-101, 100% rutile crystal, manufactured by Ishihara Techno Corporation) was dipped in an aqueous solution of 2.47 g of commercially available ruthenium chloride ($RuCl_3.nH_2O$, Ru content: 41.3% by weight) and 43.4 g of pure water, evaporated under reduced pressure at 50℃ for 4 hours, and then dried at 60℃ for 2 hours. After drying, the powder was sufficiently ground to obtain a black powder. This powder was dipped in a solution of 13.8 g of a 2N potassium hydroxide aqueous solution, 70.0 of pure water and 3.90 g of hydrazine monohydrate under nitrogen at room temperature. Bubbling occurred on dipping. The gas bubbled during the treatment for 1 hour. The reduced powder was separated by filtration. Washing was conducted for 30 minutes by adding 1000 ml of water, followed by filtration. This operation was repeated five times. To the powder separated by filtration, 50 g of a 2 mol/l of potassium chloride aqueous solution was added and, after stirring, the powder was separated by filtration again. This operation was repeated three times. The resulting cake was dried at 60℃ for 4 hours to obtain a blackish brown powder. After heating from room temperature to 350℃ in an air over 1 hour, the solid was calcined at the same temperature for 3 hours. After completion of the calcination, 1000 ml of pure water was added and the mixture was stirred and, furthermore, the powder was separated by filtration. This

operation was repeated five times and, after adding dropwise an aqueous silver nitrate solution to the wash, it was confirmed that potassium chloride is not remained. Then, 19.5 g of a black powder was obtained by drying this powder at 60℃ for 4 hours. The resulting powder was molded to adjust the particle size to 1.0～2.0 mm, thereby obtaining a ruthenium oxide catalyst supported on titanium oxide.

Incidentally, the calculated value of the content of ruthenium oxide was as follows.

$RuO_2/(RuO_2 + TiO_2) \times 100 = 6.3\%$ by weight

The calculated value of the content of ruthenium was as follows.

$Ru/(RuO_2 + TiO_2) \times 100 = 4.8\%$ by weight

In addition, the content of an OH group of the titanium oxide powder as a carrier was measured in the same manner as in Example 5 of the specification of the above-identified application. The content of the OH group was 1.69×10^{-3} (mol/g-carrier).

The ruthenium oxide catalyst supported on titanium oxide (2.5 g) thus obtained was diluted by mixing with a 10 g of spherical α- alumina carrier (2 mmϕ in size, SSA995, manufactured by Nikkato Co.) and then charged in a quartz reaction tube (inner diameter: 12 mm). A hydrogen chloride gas (192 ml/min.) and an oxygen gas (184 ml/min.) were respectively supplied under atmospheric pressure (in terms of 0 ℃, 1 atm). The quartz reaction tube was heated in an electric furnace to adjust the internal temperature (hot spot) to 299.4℃. 3.5 Hours after the beginning of the reaction, the gas at the

reaction outlet was sampled by passing it through an aqueous 30 wt% potassium iodide solution, and then the amount of chlorine formed and amount of the non-reacted hydrogen chloride were respectively determined by iodometric titration and neutralization titration.

The formation activity of chlorine per unit weight of the catalyst determined by the following equation was 3.2×10^{-4} mol/min. g-catalyst.

Chlorine formation activity per unit weight of catalyst (mol/min. g-catalyst) = amount of outlet chlorine formed (mol/min)/weight of catalyst (g)

CONSIDERATION

Dependency of the activity on the amount of OH group contained in the titanium oxide carrier before supporting the ruthenium compound, was shown in a figure attached hereto.

Herein, the contents of ruthenium contained in the catalysts of Examples 5, 14 and 15 were respectively 4.7% by weight, and that of Experiment was 4.8% by weight. Therefore, all of the contents are essentially equal. Further, the rutile content of titanium oxide used as a carrier in each of these catalysts is 100%.

Therefore, in the figure, the dependency of the activity on the amount of the OH group contained in the titanium oxide carriers, is adequately exhibited.

From the figure, it is clear that the amount of the OH group contained in the titanium oxide carrier used for the ruthenium catalyst affects on the activity of chlorine production as shown

in the figure.

In addition, this result can not be expected from Gratzel et al (U.S.Patent No. 4,847,231) cited because Gratzel et al is silent to the amount of OH group contained in titanium oxide used as a carrier.

That I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above identified application or patent issued thereon.

Signed this 23rd day of February, 2004.

Takuo Hibi

Takuo HIBI